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Technical Report No. 11

**CHEMISTRY WITHIN MOLECULAR CLUSTERS**

by

William R. Peifer, M. Todd Coolbaugh, and James F. Garvey\*

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Prepared for Publication

in

Clusters and Clustering from Atoms to Fractals

Edited by P. Reynolds

North-Holland, Amsterdam, 1990

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90 03 28 031

## REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION <b>Unclassified</b>			1b RESTRICTIVE MARKINGS	
2a SECURITY CLASSIFICATION AUTHORITY			3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited	
2b DECLASSIFICATION/DOWNGRADING SCHEDULE				
4. PERFORMING ORGANIZATION REPORT NUMBER(S) <b>Technical Report # 11</b>			5 MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION <b>SUNY/Buffalo</b>		6b OFFICE SYMBOL (If applicable)		7a NAME OF MONITORING ORGANIZATION <b>Office of Naval Research</b>
6c. ADDRESS (City, State, and ZIP Code) <b>Dept. of Chemistry, Acheson Hall, SUNY/Buffalo, Buffalo, NY 14214</b>			7b ADDRESS (City, State, and ZIP Code) <b>Chemistry Program 800 N. Quincy St., Arlington, VA 22217</b>	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION <b>Office of Naval Research</b>		8b OFFICE SYMBOL (If applicable)		9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER <b>#N00014-88-K-0483</b>
8c ADDRESS (City, State, and ZIP Code) <b>Chemistry Program, 800 N. Quincy St., Arlington, VA 22217</b>			10 SOURCE OF FUNDING NUMBERS	
			PROGRAM ELEMENT NO	PROJECT NO
			TASK NO	WORK UNIT ACCESSION NO
11 TITLE (Include Security Classification) <b>CHEMISTRY WITHIN MOLECULAR CLUSTERS</b>				
12 PERSONAL AUTHOR(S) <b>William R. Peifer, M. Todd Coolbaugh and James F. Garvey</b>				
13a TYPE OF REPORT <b>Technical</b>		13b TIME COVERED FROM _____ TO _____		14 DATE OF REPORT (Year, Month, Day)
15 PAGE COUNT				
16 SUPPLEMENTARY NOTATION <b>Clusters and Clustering from Atoms to Fractals; North-Holland, Amsterdam, 1990</b>				
17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP		
19 ABSTRACT (Continue on reverse if necessary and identify by block number)				
<p>↙ This article reviews our cluster work for the past three years at SUNY. We document with illustrative examples, chemical reactions which only occur within the solvating environment of a cluster.</p> <p><i>Sciences: Periodical, military Publications, Scientific Literature; Reports. (EG)</i></p>				
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION <b>Unclassified</b>	
22a NAME OF RESPONSIBLE INDIVIDUAL <b>Dr. David L. Nelson</b>			22b TELEPHONE (Include Area Code) <b>(202) 696-4410</b>	22c OFFICE SYMBOL

## **Chemistry within Molecular Clusters**

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### **A) Introduction**

A subject of great interest in recent years has been the study of the physics of weakly bound van der Waals clusters. These species have been probed in a variety of ways to gain an understanding of their formation and to determine their various physical properties. However, the study of chemical reactions within clusters is especially intriguing since clusters can bridge the disparate fields of bimolecular gas-phase reaction dynamics and solution chemistry. The ultimate goal of these studies is to obtain an understanding of the factors that govern reactions in solution but which are absent in gas phase processes. By concentrating on the chemistry within these cluster systems it is possible to directly learn how the behavior of the system changes as a function of stepwise solvation.

Most of the recent work in this area consists of utilizing the neutral cluster as one of the reagents for a bimolecular reaction<sup>1-8</sup> with the product cluster ion being directly detected via conventional mass spectrometric techniques. Apart from the observation of protonated clusters {i.e.,  $(\text{H}_2\text{O})_n\text{H}^+$ ,<sup>9</sup>  $(\text{NH}_3)_n\text{H}^+$ ,<sup>10,11</sup>  $(\text{CH}_3\text{COCH}_3)_n\text{H}^+$ ,<sup>12</sup>  $(\text{CH}_3\text{OH})_n\text{H}^+$ ,<sup>13</sup>  $(\text{CH}_3\text{OCH}_3)_n\text{H}^+$ ,<sup>13</sup> and a few heterocluster ions such as  $[(\text{ROH})_n(\text{H}_2\text{O})_m]\text{H}^+$ <sup>14,15</sup> and  $[(\text{CH}_3\text{OH})_n(\text{H}_2\text{O})_m]\text{H}^+$ ,<sup>16</sup>} there are few reported cases of chemical reactions taking place within the cluster ion itself.<sup>12,16-20</sup> Yet it has been known that electron impact ionization of clusters leads to ions that closely resemble many of the intermediates found in bimolecular ion-molecule reactions.<sup>21,22</sup>

In addition to this typical unimolecular and bimolecular gas-phase chemistry already studied within clusters, our group has recently observed the generation of new cluster product ions which cannot be explained by either of these two known processes. That is, we observe product ion formation that has absolutely no counterpart with gas-phase bimolecular reactions and which only occurs within a van der Waals cluster<sup>23</sup>. These new processes, which we have begun to document in the past three years at SUNY, include the generation of  $(\text{C}_2\text{H}_4\text{F}_2)_{n>4}\text{H}^+$  ions from 1,1-difluoroethane clusters<sup>24</sup>, the generation of  $(\text{CH}_3\text{OCH}_3)_n\text{CH}_3\text{OH}_2^+$  &  $(\text{CH}_3\text{OCH}_3)_n\text{H}_3\text{O}^+$  ions from dimethyl ether clusters<sup>25,26</sup>, the generation of  $(\text{NH}_3)_n\text{N}_2\text{H}_8^+$  ions from ammonia clusters<sup>27</sup> and

the photogeneration of  $\text{MoO}^+$  and  $\text{MoO}_2^+$  ions from van der Waals clusters of molybdenum or tungsten hexacarbonyls<sup>28</sup>. The observation of these new chemical processes which occur only within a cluster, is particularly exciting for chemists in that we may now utilize clusters as a novel "crock-pot" in which to produce new molecules, which could not be produced by any other means.

Thus, while the study of reactive processes in clusters may be used as a bridge between the gas-phase "bimolecular" and the "solvated multimolecular" world of chemical reactions in solution, we feel that this bridge has in fact turned into a crossroads. That is we have demonstrated new chemical reactions and unexpected dynamics which can occur only within the condensed environment of a molecular cluster. We will now show illustrative examples wherein this new chemistry within clusters occurs through either:

- 1) stabilizing unstable reagents
- 2) stabilizing unstable intermediates
- 3) providing new chemical pathways

## **B) Experimental Section**

The majority of our experiments consist of generating a beam of neutral van der Waals clusters and then, by electron impact, performing mass spectroscopy on the cluster species within the beam. Though the cation within the cluster is rapidly generated ( $\sim 10^{-14}$  s), it takes microseconds before the resulting cluster ion is mass selected by the quadrupole filter. On this lengthy time scale the cation within the cluster may rid itself of its excess energy either by fragmentation, evaporation of neutral monomers or the solvated cation may chemically react with one (or more!) of the solvating neutrals. In any case, a new product cluster ion has been generated, which is then detected via mass spectroscopy.

One may visualize the electron impact ionizer of our mass spectrometer as a 'reaction cell' in which the precursor cluster ion is generated and allowed to 'incubate' for microseconds, and then the newly generated product ions are subsequently analyzed via mass spectroscopy. By observing the distribution of product cluster ions in the mass spectra we can then deduce the ion-molecule chemistry which is occurring within the bulk cluster, and observe how this chemistry changes as a function of cluster size.

Our molecular beam apparatus consists of a Campargue-type beam source and has been described previously<sup>29</sup>. The cluster beam is generated from a neat expansion through a 250  $\mu\text{m}$  orifice. The mass spectrometer is an Extrel C-50 (200 W, 3/8" diameter rods, open design ionizer) capable of unit mass resolution and uniform sensitivity up to  $m/z = 1400$ . During beam operation the

pressure in the mass spectrometer chamber was kept below  $5 \times 10^{-7}$  torr.

For the metal hexacarbonyl experiments (section C-3-b) a different beam apparatus is used. Helium, seeded with a metal carbonyl compound at its room temperature vapor pressure (typically a few hundred mTorr), is admitted into the low-volume stagnation region of a Newport BV-100 pulsed molecular beam valve fitted with an end plate having a 0.5 mm diameter,  $30^\circ$  conical aperture. Metal hexacarbonyl van der Waals complexes are then formed in the free-jet expansion of the pulsed beam of seeded helium. Operation of the valve at 1 Hz leads to maximum chamber pressures of about  $3 \times 10^{-6}$  Torr. The cluster beam pulse is directed axially into the ion source of a Dycor M200M quadrupole mass spectrometer, where it is intersected by the focused output from a Lambda Physik EMG 150 excimer laser, operated on the KrF\* transition at a pulse energy of ca. 100 mJ. Synchronization of the laser and the molecular beam valve is accomplished through the use of an external timing circuit with an adjustable delay.

### C) Results and Discussion

#### 1) Stabilizing an Unstable Reagent within the Solvating Confines of a Cluster

##### 1,1-Difluoroethane Clusters<sup>24</sup>

The dominant reactive process which occurs within cluster ions consists of a bimolecular reaction between the monomer cation and one of the neutral solvent molecules generating a protonated cluster ion and a radical. This reaction has been well studied in a variety of bimolecular gas phase experiments and is observed to occur for a wide range of molecules. In many cases these reactions are highly exoergic and quite facile. Therefore, a molecular cluster mass spectrum is usually dominated by the appearance of cluster ions with the empirical formula  $M_nH^+$  (where M is the monomeric unit).

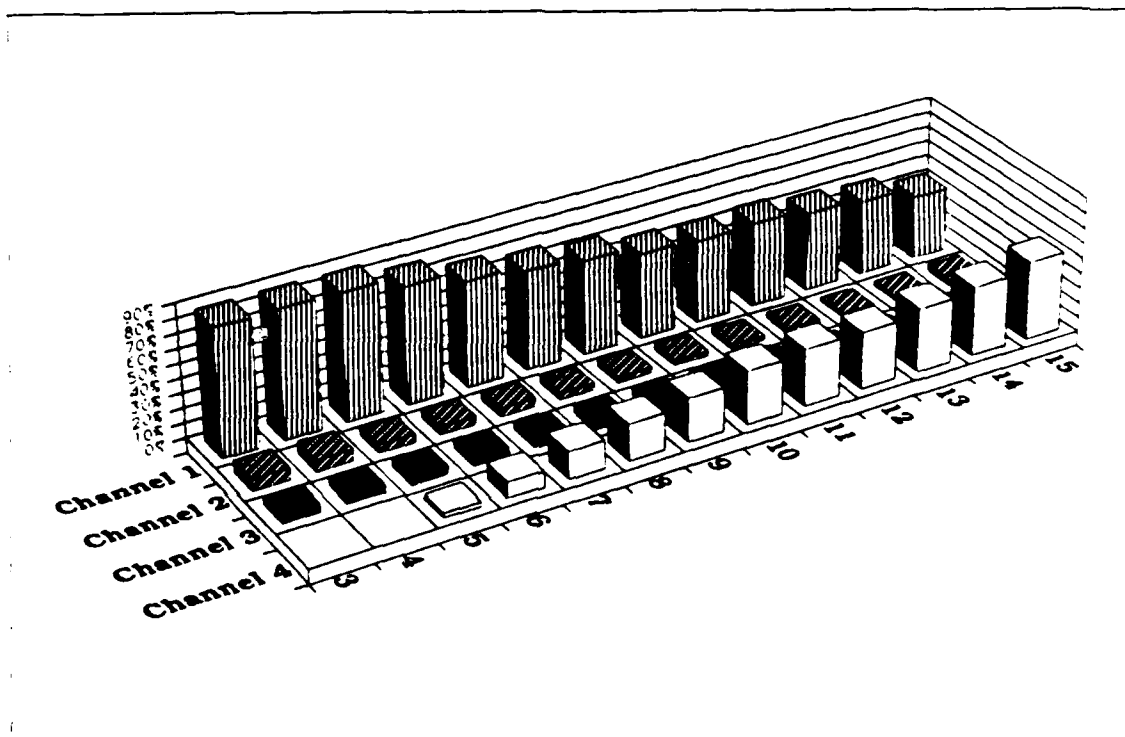
However, for many organic molecules, upon electron impact ionization, the parent ion is unstable. That is the ground state cation ( $M^+$ ) is thermodynamically unstable with respect to fragmentation. In such cases the mass spectrum is then composed solely of fragment ions, and identification of the molecule must be made by the characteristic fragmentation pattern.

The mass spectrum of 1,1-difluoroethane (DFE) represents just such a case. Since the parent ion is unstable, we expect that the reaction



will not occur within the  $(C_2H_4F_2)_n$  cluster, since the parent ion never survives long enough to react with one of the solvating monomers. Hence, the cluster mass spectrum of DFE should have a complete absence of peaks with the formula  $M_nH^+$ , and be composed solely of solvated fragment ions.

Figure 1 below shows a 100 eV mass spectrum of DFE clusters as a function of cluster size and process channel (i.e., channel 1:  $M_nCH_3CFH^+$ , channel 2:  $M_nC_2H_3F^+$ , channel 3:  $M_nC_2H_3F_2^+$ , and channel 4:  $M_nH^+$ ). We see in Figure 1 that in addition to the expected fragmentation (channels 1-3) another sequence of peaks which have the empirical formula of  $M_nH^+$ , appear at  $n \geq 5$  and continues to become progressively more prominent with increasing cluster size. This is in direct contrast to the fragment channels which monotonically decrease with increasing cluster size.



**Figure 1: Percent yield of cluster ion as a function of n and process channel**

As Jungen and co-workers point out<sup>30</sup>, a parent ion might be observed as a metastable ion if it is formed in the Franck-Condon region of the neutral molecule. Thus, if the parent ion is generated within the cluster, the presence of solvating molecules may stabilize it long enough, such that it can react with one of the neutral monomers by reaction 1. The fact that the protonated cluster ions only appear for  $n \geq 5$ , suggests that  $M_6^+$  is the critical size for stabilizing the monomer ion, in the absence of any monomer evaporation. However should any evaporation occur, it will only shift rows relative to each other, and not affect the qualitative conclusions which we draw from the analysis, that an unstable reagent cation can be stabilized within a cluster long enough so it can undergo reactions with the solvating monomers. We hope to further study other fluorinated hydrocarbon systems in order to better understand the systematics.

## 2) Stabilizing an Unstable Intermediate within the Solvating Confines of a Cluster Dimethyl Ether Clusters<sup>25,26</sup>

The bottom of Figure 2 shows a typical 70 eV electron impact mass spectrum for  $(\text{CH}_3\text{OCH}_3)_n$  clusters extending from the dimer to the trimer. In addition to the expected protonated cluster peaks there are additional peaks corresponding to the hydronium ion (which has been reported before<sup>25</sup>) and protonated methanol ions, solvated by 2 dimethyl ether (DME) molecules. This sequence of cluster peaks is observed throughout the entire cluster mass spectrum to the limit of our sensitivity ( $n = 28$ ).

It is interesting to note that while the  $\text{CH}_3^+$  &  $\text{CH}_3\text{OCH}_2^+$  fragment cations are extremely intense in the monomer mass spectrum of DME (~ 54% of all ion intensity), the same cluster cations are substantially reduced in intensity (i.e.  $(\text{DME})_n\text{CH}_3^+$  &  $(\text{DME})_n\text{CH}_3\text{OCH}_2^+$ ). We speculate that this is due to the fragments being consumed by an ion-molecule reaction within the cluster. One likely candidate is the ion-molecule reaction of the fragment cations with a neutral DME, within the bulk cluster to form a trimethyloxonium cation intermediate. This type of ion-molecule reaction has been previously observed by Harrison and Young through the use of a tandem mass spectrometer<sup>31</sup>. This newly formed trimethyloxonium cation may then undergo a rearrangement to form the observed products. This mechanism is shown in Figure 2.

This mechanism is similar to that observed for the decomposition of DME over zeolite catalysts. van Hooff, *et al.*<sup>32</sup> observed that conversion of DME over a zeolite catalyst produced ethylene and propene as primary olefins. To account for their results they invoke a trimethyloxonium intermediate as the common intermediate for the observed products. We therefore speculate that the DME cluster reactions leading to the same products, should involve the same mechanism found to occur on zeolite catalysts. That is, within the stabilizing environs of a cluster, the trimethyloxonium cation may internally rearrange where it then forms protonated methanol (via elimination of ethylene) or protonated water (via elimination of propene).

This analogous process has previously been reported for the collisional activation of the monomer  $(\text{CH}_3)_3\text{O}^+$  ion<sup>33</sup>. However recent additional work appears to be at variance with that original result<sup>34</sup>. This variance we feel is due to the thermodynamic instability of the bare  $(\text{CH}_3)_3\text{O}^+$ . That is for the isolated  $(\text{CH}_3)_3\text{O}^+$ , unimolecular dissociation can now effectively compete with the rearrangement reaction, and only simple methyl loss is observed. However, within the solvating environs of a cluster (or a zeolite surface), this unstable intermediate may be stabilized on a long enough time scale, to now allow it to undergo this rearrangement reaction, to then form the observed products.

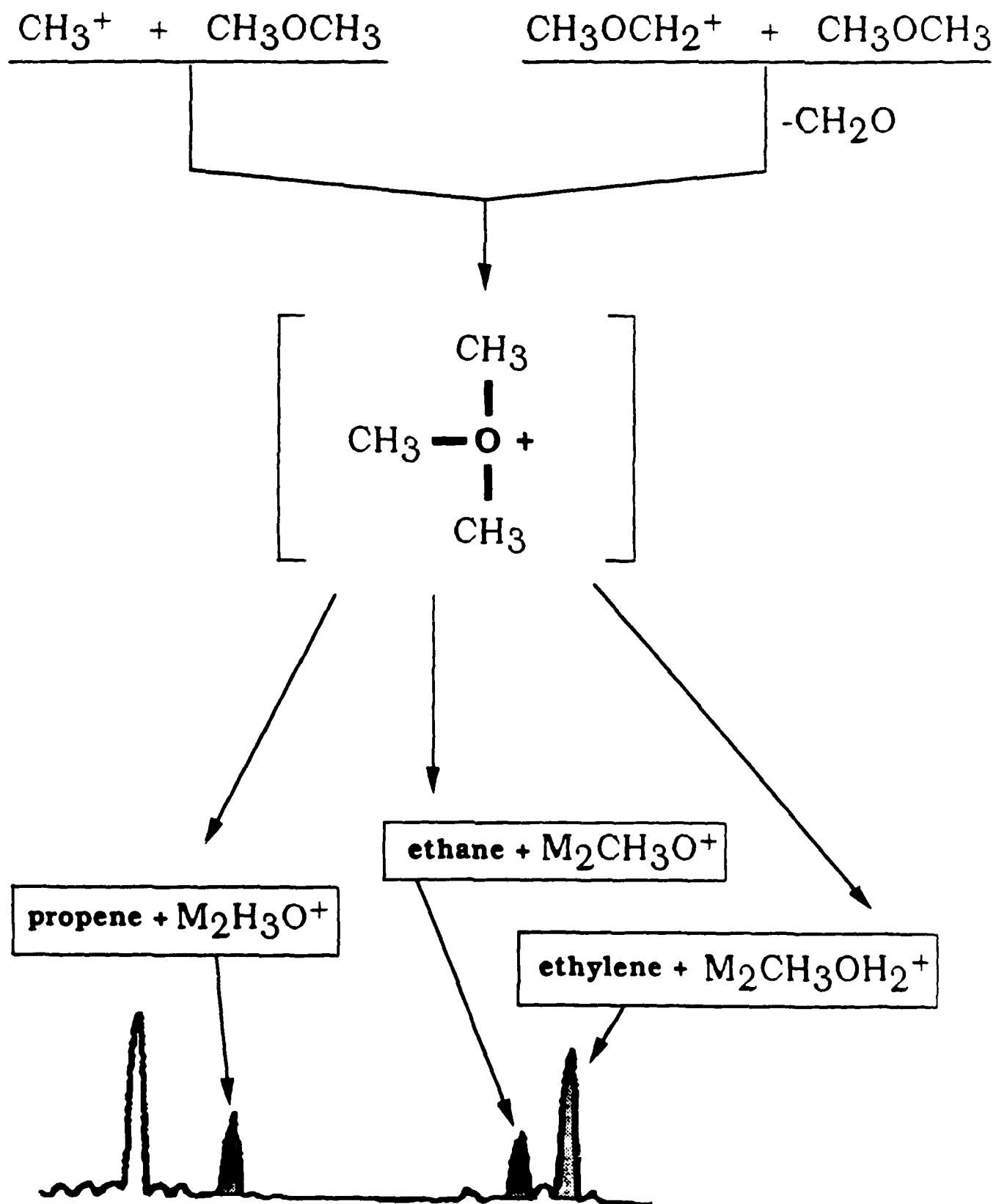


Figure 2: Proposed reaction mechanism for observed cluster ions



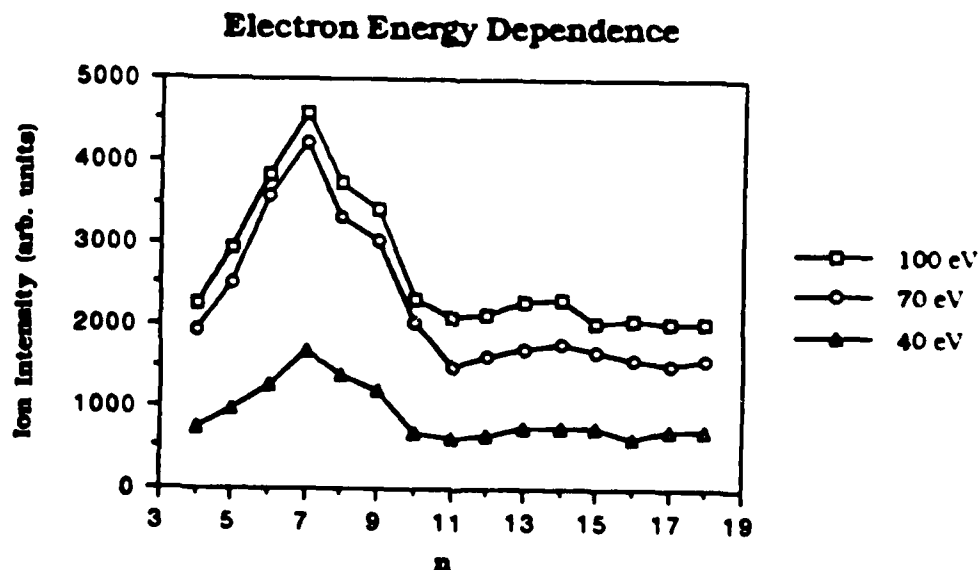
### 3) Providing New Chemical Pathways

#### a) Ammonia Clusters<sup>27</sup>

The ammonia cluster mass spectrum has been widely studied<sup>10,11</sup>, and is dominated by a sequence of peaks with the empirical formula  $(\text{NH}_3)_n\text{NH}_3^+$  and  $(\text{NH}_3)_n\text{NH}_4^+$ , corresponding to the already discussed protonation reaction. Careful study of the mass spectrum also reveals another series of peaks which at first glance appears to have the empirical formula  $(\text{NH}_3)_n\text{NH}_2^+$ . That is they result from the process of the fragmentation of a N-H bond in the  $\text{NH}_3^+$  cation, generating the  $\text{NH}_2^+$  fragment intact within the cluster.

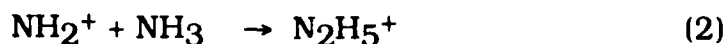
A plot of the relative intensities of the  $(\text{NH}_3)_{n-1}\text{NH}_2^+$  ions as a function of cluster size ( $n$ ) is shown in Figure 3, for a variety of electron energies. A magic number, corresponding to an enhancement in the ion signal, is clearly observed for the cluster ion of size  $n=7$ . This result is independent of electron energy, or cluster expansion conditions. We feel then that this intensity distribution is due solely to the large stability of the  $(\text{NH}_3)_6\text{NH}_2^+$  cluster ion.

This is a very surprising result in that magic numbers<sup>10,11</sup> {i.e.,  $(\text{NH}_3)_4\text{NH}_4^+$ } usually result from the closing of the first solvent shell around the central cation. If the central cation in this case is indeed  $\text{NH}_2^+$ , why does the first solvent shell closure need 6 ammonia? Why wouldn't 2 or 3 ammonia's suffice?



**Figure 3: Intensity of  $(\text{NH}_3)_{n-1}\text{NH}_2^+$  vs. cluster size**

We can account for the observed size dependence of the  $(\text{NH}_3)_n\text{NH}_2^+$  cluster ion yield if we assume that an associative ion-molecule reaction occurs between the nascent  $\text{NH}_2^+$  ion and an adjacent  $\text{NH}_3$  solvent molecule within the cluster:

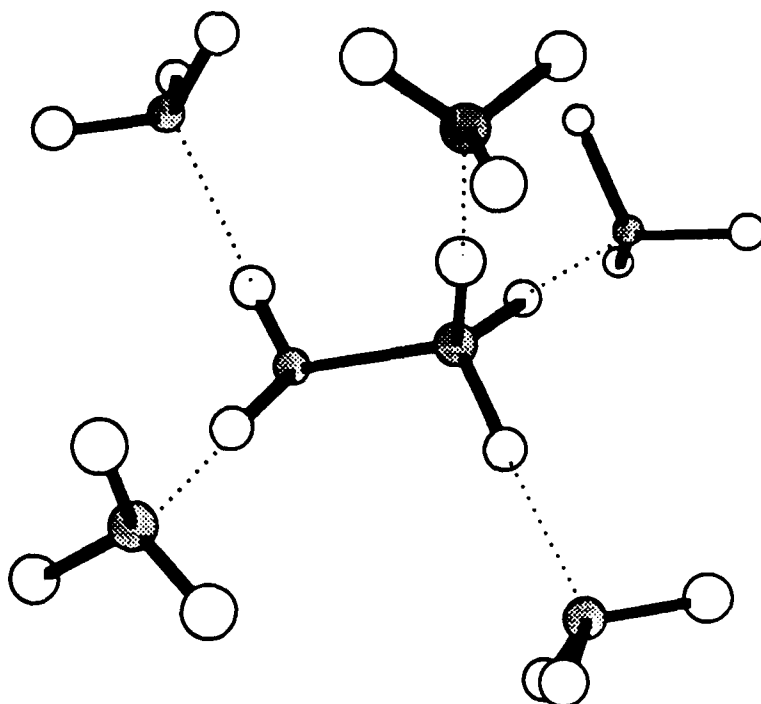


From available thermochemical data,<sup>35</sup> we estimate that this reaction is exothermic by 4.52 eV. A similar (albeit endothermic) bimolecular reaction is known to occur between  $\text{NH}_3^+$  and  $\text{NH}_3$ :



at a rate which is about 0.1% of gas-kinetic.<sup>36</sup> We expect the barrier for reaction (2) to be smaller than that for reaction (3) for the following reasons. First, within the context of the Hammond postulate,<sup>37</sup> the barrier to reaction (2) is expected to occur earlier along the reaction coordinate, the potential surface is expected to be more attractive, and the transition state is expected to more closely resemble the reactants. Second, the activation energy for reaction (2) is expected to be lower than that of reaction (3), since the transition state for (3) must contain at least one highly extended N-H bond (correlating with eventual loss of the product H atom). By analogy with other associative bimolecular reactions, we would expect the activation energy for reaction (2) to be small, if not negligible, and determined to a great extent by the dipole-dipole interaction. We might therefore expect, based on differences in activation energies and Arrhenius A factors, that the associative reaction (2) will proceed at a rate significantly greater than 0.1% of the gas-kinetic rate.

While the "naked" (unclustered) product of the highly exothermic associative reaction (2) would have sufficient internal energy to undergo subsequent N-H bond cleavage, it would certainly be stabilized through solvation by additional  $\text{NH}_3$  molecules. In fact, if we hydrogen-bond five  $\text{NH}_3$  solvent molecules to the five H atoms of the  $\text{N}_2\text{H}_5^+$  product ion, we end up with an ion having a completed solvation shell with the anticipated empirical formula,  $(\text{NH}_3)_6\text{NH}_2^+$ . The  $(\text{NH}_3)_5\text{N}_2\text{H}_5^+$  structure is illustrated in Figure 4. This cluster ion has a total of seven nitrogen atoms and accounts for our observation of a magic number,  $n=7$ . It is expected that the exothermicity of reaction (2) should enhance the magic number effect, since this excess heat will serve to "boil off" the loosely bound solvent molecules which are not in the first solvent shell. This is an interesting example wherein the observation of magic numbers, was necessary to elucidate the true chemical identity of the central cation.



**Figure 4: Proposed structure for  $(\text{NH}_3)_{n-1}\text{NH}_2^+$  cluster ion.**

#### **b) Metal Hexacarbonyl Clusters**

Van der Waals clusters of  $\text{M}(\text{CO})_6$  ( $\text{M}=\text{Mo}, \text{W}$ ) generated in the free-jet expansion of a pulsed beam of seeded helium are subjected to multiphoton ionization (MPI) and the product ions analyzed by quadrupole mass spectrometry. These species are of fundamental significance in our understanding of metal-metal and metal-ligand bonding interactions, and can serve as model systems for the study of catalysis and surface phenomena. Studies of the effects of cluster size and structure on reactivity of transition metal carbonyl clusters can provide us the necessary database with which to test and refine our theories concerning the chemistry and physics of bulk metals.

The multiphoton dissociation and ionization dynamics of mononuclear and covalently bound multinuclear transition metal carbonyls is well understood: initial multiphoton dissociation (MPD) of the metal carbonyl results in complete ligand stripping, leaving behind a naked metal atom which is subsequently

photoionized. Consequently, the 248 nm. MPI mass spectrum for the  $M(CO)_6$  monomer is dominated almost exclusively by the  $M^+$  cation signal.

On the other hand, the multiphoton photophysics of van der Waals complexes of transition metal carbonyls is not so thoroughly characterized. Indeed, for MPI of  $\{M(CO)_6\}_n$  clusters, we observe not only the production of  $M^+$  but the oxide ions;  $MO^+$  and  $MO_2^+$ . Observing the production of these ions as a function of laser intensity reveals that the yield of  $M^+$  depends on the square root of laser intensity, while the yields for both of the oxide ions are found to be nearly independent of laser intensity (6-210 mJ). This strongly suggests that the mechanism leading to production of  $M^+$  remains sensitive to laser intensity over the range of intensities investigated, while the mechanism leading to production of the metal oxide ions is nearly saturated within this range of intensities. Therefore, we conclude that we are probably observing two distinct processes. The first is a multiphoton dissociation within the cluster leading to a bare metal atom which is subsequently ionized via MPI, generating the  $M^+$  ion signal. The second process is a photochemically induced intracuster reaction leading to oxomolybdenum ions

We propose that a novel binuclear adduct arises thru an intracuster reaction and that the oxide ions arise thru subsequent photoionization and fragmentation of that adduct. That is, within the cluster, the photogenerated metal atom can associate with the ligands of an adjacent metal carbonyl "solvent" molecule. We therefore propose, on the basis of orbital symmetry considerations, that the nascent metal "photoatom" interacts with a neighboring metal carbonyl "solvent molecule" via two such bridging carbonyls to form a stable six member structure. Then through back-donation of metal  $d_{xy}$  electron density to the empty  $\pi^*$  MO's of the carbonyl ligands, the 2 C-O bonds weaken and break, eventually resulting in the observed oxide ion formation.

However, we find no evidence of such behavior in the  $Cr(CO)_6$  system. Based on these results for the group VI B heacarbonyls, we suggest that the reactivity within clusters, of first-row transition metal atoms is fundamentally different from that of second- or third-row metals and is determined by the occupancy and relative size of the metal d orbitals. Based on our model we would predict that the intracuster reaction between a photogenerated metal atom and an adjacent  $M(CO)_6$  cluster molecule depends explicitly on the efficient overlap of the relevant molecular orbitals. In the particular case of Cr, the small d orbital on the metal makes for poor overlap with the carbonyl ligands, hence the lack of reactivity. This model, which invokes different modes of CO coordination, may have important implications for the study of catalysts.

#### D) Future Directions

The four examples just shown represent a small sampling of the new cluster chemistry which we have recently observed<sup>38</sup>. We feel this is only the beginning in terms of the new chemistry which can be discovered within clusters. New directions include the use of mass selected cluster beams to directly observe the reaction dynamics, and attempts to spectroscopically probe, via laser induced fluorescence, the internal states of the radical product generated within the cluster.

An new extrapolation of this work is to use clusters to generate novel bulk materials in the form of thin films. We have currently modified the standard Smalley metal cluster source, to be used for just such thin film generation. Preliminary experiments have shown that this source is capable of generating a high temperature material within a beam expansion and depositing that material at a cool substrate. We hope that by tailoring the expansion conditions a variety of high quality homogenous thin films can be produced with obvious industrial applications (superconducting thin films, diamond-like carbon thin films, patterned or multi-layered thin films, etc...).

Lastly, we hope to utilize our knowledge concerning the generation of new product cluster ions, to alter or modify already existing surfaces. That is, for many of the reactions we have studied, metastable reactive intermediates are generated within the cluster. These highly reactive species may be ideal for use as selective surface etchants, or even for CVD type deposition onto a substrate.

#### E) Acknowledgements

This research was supported by the Office of Naval Research which is hereby gratefully acknowledged.

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